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LOW ENERGY EXPANSION OF THE SCATTERING AMPLITUDE FOR LONG RANGE QUADRUPOLE POTENTIALS

By

Thomas F. O'Malley

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Low Energy Expansion of the Scattering Amplitude for Long Range Quadrupole Potentials*

Thomas F. O'Malley

Joint Institute for Laboratory Astrophysics
Boulder, Colorado

For static potentials which are proportional asymptotically to \( q P_2(\cos \theta)/r^3 \), the low energy expansion of the scattering amplitude is found through terms of \( O(k) \), using a modification of the method developed by Levy and Keller for central potentials. The resulting expansion to lowest order in \( k \) is found to be \( f(\theta, \phi) \sim -A + (q/3) P_2(\cos \theta_K) + O(k) \), where \( A \) is the scattering length and \( \theta_K \) is the coordinate of the momentum transfer vector. Applications are attempted first to electron-atom elastic scattering where results are somewhat more complicated than for the potentials above, secondly to transitions between magnetic quantum states of atoms caused by slow electrons.

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1. INTRODUCTION

Effective range expansions developed originally for short ranged potentials have been extended in recent years first to spherical potentials with \( r^{-4} \) tails and finally to potentials with arbitrary \( r^{-n} \) radial dependence asymptotically. This has enabled the usefulness of the low energy expansion to be extended to electron-atom collisions, and to any scattering problem where long range van der Waals forces are operative. However there are physical problems, exemplified by the scattering of electrons from atomic oxygen or other non-symmetric atoms, for which the asymptotic form of the interaction is not the \( r^{-4} \) polarization potential but rather the quadrupole interaction proportional to \( r^{-3} p_2(\cos \theta) \); in particular:

\[
(2m/h^2) V(r) \sim q p_2(\cos \theta)/r^3 - r^{-4}[p + \dot{p} p_2(\cos \theta)] + O(r^{-5})
\]

(1.1)

Since such a potential is not spherically symmetric, the usual phase shift analysis is not applicable for one has a coupling of different angular momentum states. Hence the expansions of Levy and Keller for the phase shifts are not applicable. But while phase shifts for this problem are not well defined, the scattering amplitude, \( f(\theta, \phi) \) is. In this paper we will look for an energy expansion for \( f(\theta, \phi) \), adapting to this purpose the approach which was used by Levy and Keller, (LK) to expand \( \tan \eta \) for symmetric potentials.

In Sec. 2, we shall briefly review the LK method, modifying it to a more heuristic form which we find easier to apply to the present purpose. In Sec. 3, the method is then applied to expanding the amplitude, \( f(\theta, \phi) \), for potentials with the asymptotic form (1.1). The dipole potential is also
briefly considered. Sec. 4 is devoted to considering the relation of the
results of the previous section to the electron-atom scattering problem. In
particular, the derivation of the form (1.1) of the potential is indicated
and the relation of \( q \) to the atom's quadrupole moment is discussed. It is
seen that the electron-atom problem is somewhat more complicated, due to the
possibility of atomic transitions from one magnetic quantum state to another.
The amplitude for these transitions is obtained to lowest order in the energy.
2. MODIFIED LEVY - KELLER METHOD

To introduce the method which will be applied in Sec. 3, consider the L = 0 scattering of a particle by a long range central potential, \(U(r)\), proportional to \(r^{-n}\) asymptotically. Levy and Keller's starting point in attacking this problem was the first order non-linear equation\(^6\) for the phase shift

\[
\frac{d}{dr} \tan \eta(r) = -k^{-1} U(r) \left[ \sin(kr) + \tan \eta(r) \cos(kr) \right]^2
\]  

(2.1)

with boundary condition \(\eta(0) = 0, \eta(\infty)\) is the desired phase shift. They then represented \(\tan \eta\) as a series in odd powers of \(k\)

\[
\tan \eta(r) = k \sum_{j=0}^{\infty} k^{2j} t_j(r)
\]  

(2.2)

Eq. (2.2) is substituted into (2.1) and equating like powers of \(k\) gives the equations for each of the \(t_j(r)\). \(t_0(\infty)\) is the negative of the scattering length, \(A\). Its equation is found to be

\[
\frac{dA}{dr} = U(r) \left[ r - A(r) \right]^2
\]  

(2.3)

where we have changed the symbol \(t_0\) to \(-A\). The equations for \(t_1\), etc. are similarly found.\(^3\) If the potential were of short range, the problem would be finished, with the \(t_j(\infty)\) furnishing the desired expansion of \(\tan \eta\). However, for long range potentials, which are proportional asymptotically to \(r^{-n}\), it is found that at most the first few of the \(t_j\) tend to a finite limit as \(r^{\infty}\). For example, if \(n = 4\), only \(t_0(\infty)\) exists. [It should be pointed out for later reference that all the quantities \(t_j(r)\) are still well defined for any finite \(r\), and the expansion, Eq. (2.2) is still meaningful. One is merely prevented from going to the limit.]

Levy and Keller's procedure at this point was to consider the difference, \(\tan \eta(r) - k \sum_{j=0}^{m} k^{2j} t_j(r) = \eta_\infty(r, k)\), where \(t_m\) is the last one whose limit is finite. Upon substituting this into (2.1), an equation for the
function \( \beta \) was derived. This equation was then solved by an iteration or perturbation approach. It was found that, to lowest order in \( k \), \( \beta \) was determined by the asymptotic region \( r \to \infty \). In this region, the usefulness of the iteration method arises from the fact that successive iterations produce successively higher powers of \( k \), so that a series in powers of \( k \) tends to fall out immediately.

For the purposes of this paper, a somewhat heuristic version of this method will be employed. We shall use the perturbation approach from the very beginning, and work directly with \( \tan \eta \), rather than introduce the difference function, \( \beta(r) \). The result of this is a greater directness and brevity, and a more intuitive approach. This will be done at the expense of introducing certain anomalous terms into the results, which however we shall see to have a clear interpretation.

To begin, let us rewrite Eq. (2.1) in integral form

\[
\tan \eta(r) = \tan \eta(R) - k^{-1} \int_R^r U(r) \left[ \sin(kr) + \tan \eta(r) \cos(kr) \right]^2 \, dr.
\]

(2.4)

\( R \) will be taken to be any very large but fixed distance (independent of \( k \)) and we vary \( k \) so that \( kr > 0 \). The region \( r < R \) is described by Eq. (2.2), as already pointed out. Now since \( R \) may be taken to be arbitrarily large, the integral may be considered to be a very small quantity for any allowable potential. (It is shown below that this imposes the mild restriction that \( r^2 U \) approach zero.) Thus the aptness of a perturbation approach to Eq. (2.4) for \( r > R \) is clear.

Since \( R \) is arbitrarily large, we substitute for \( U(r) \) its asymptotic expansion, \( U(r) \sim \sum_n U_n r^{-n} \). We further introduce the new variable \( kr = x \). Eq. (2.4) then becomes

\[
\tan \eta(r) = \tan \eta(R) - \sum_n k^{n-2} \int_0^{kr} dx \, x^{-n} \left[ \sin(x) + \tan \eta \cos(x) \right]^2.
\]

(2.5)
If we temporarily ignore the $k$ dependence of the lower limit of integration, the way in which the various terms in the asymptotic expansion of $U$ contribute to the energy expansion of $\tan \eta$ follows by inspection from Eq. (2.5). In applying perturbation theory, one first takes $\tan \eta$ as the zeroth order quantity and substitutes this for $\tan \eta$ on the right hand side of Eq. (2.5). From Eq. (2.2), we see that this quantity is $O(k)$. In first order perturbation theory then, each $r^{-n}$ term in $U$ contributes a $k^{n-2}$ term to $\tan \eta$ plus terms of higher order. Now when these first order terms are substituted back into the integral on the right hand side, they produce in second order an additional factor $k^{n-2}$; and so provided the lowest $n, n_o$, is greater than 2, the leading term in second order perturbation theory is $O[k^{2(n_o - 2)}]$, and so on, just as found in LK. It is in this property that the power of the method lies. However, because of the $k$ dependence of the lower limit of integration, there will be additional lower order terms in the total result.

We now proceed to study these terms and illustrate the method at the same time by solving for $\tan \eta(m)$ in first order, for a potential with $n_o = 4$, the case which LK treated in detail. We assume for convenience that there are no other terms in the asymptotic expansion, and look for terms of order less than $k^3$. It will be seen that all the terms found by LK are reproduced very simply. In the zeroth order, we set for $r \geq R$

$$\tan \eta^{(0)}(r) = \tan \eta(R) = -A(R) k + O(k^3) \quad (2.6)$$

where the second equality follows from Eq. (2.2) with the notation $A = -t_o$. (This equation, as mentioned above, is valid up to any $R$ which is fixed and finite.) Substituting this in the appropriate places on the right hand side of Eq. (2.5) gives for the first order result

(6)
\[
\tan \eta^{(1)}(\infty) = -A(R)k - U_4k^2 \int_{kR}^{\infty} \left[ \sin x - A(R)k \cos x \right]^2 x^{-4} dx + O(k^3)
\]

\[= -[A(R) + \frac{U_4 A(R)}{R^2} + \frac{U_4 A^2(R)}{3R^3}]k + \frac{1}{3} \frac{U_4}{10} k^2 \]

\[+ \frac{4}{3} U_4 A(R) k^3 \ln k + O(k^3) \quad . \tag{2.7}
\]

The integrals, which are elementary, are simplified if one notices that with the exception of the \( k^2 \) term all other terms come from the singularities at the lower limit of integration. [In all this analysis, since \( R \) is fixed, the quantity \( kR \) is considered an infinitesimal.] If one compares the result, Eq. (2.7), with the corresponding result Eq. (35) of \( Lk^3 \) which is likewise first order, one sees that they are essentially the same. The only difference is that their \( \eta_0 \), (the negative of the scattering length) is replaced by the bracket term in the present result. A moment's reflection shows in what sense they are the same, namely the bracket represents the beginning of a perturbation expansion of \( A \), starting with \( A^{(0)} = A(R) \) in Eq. (2.3).

This was to be expected since we are using a perturbation method throughout. I can be verified explicitly if one looks for the solution of Eq. (2.3) in first order perturbation theory with the present potential. This is given by

\[
A^{(1)}(\infty) = A(R) + U_4 \int_{R}^{\infty} [r - A(R)]^2 r^{-4} dr
\]

which when evaluated is exactly equal to the bracketed quantity in Eq. (2.7).

These perturbation corrections to \( A(R) \) are easily recognized in a calculation like Eq. (2.7) first by their \( k \) dependence and secondly by their explicit dependence on \( R \). What they amount to is a renormalization of our zeroth
order scattering length. [If we had kept higher powers of $k$, there would have been renormalizations of the effective range as well.] The other terms in Eq. (2.7), the $k^2$ and $k^3 \ln k$ terms, are quite independent of the choice of $R$. Our practice in applying the method hereafter will be to replace, in all final results, both terms like the bracket term in Eq. (2.7) and quantities like $A(R)$ in the log term by the fully renormalized quantity $A = A(\infty)$, to which they tend as either $R \to \infty$ or the order of perturbation theory is increased.

Since the method just described is to be used in the following section to find the expansion of the scattering amplitude, a brief review of the procedure may be in order. One first finds the exact first order non-linear equation for the quantity $f$ of interest corresponding to Eq. (2.1) above and writes it in integral form as in Eq. (2.4). One then considers the region $r$ less than some large but fixed $R$, and makes the expansion corresponding to Eq. (2.2) for $f(R)$. Since this is the same whether the potential is short or long ranged, the form of the expansion will usually be known already. However it is very simply derived by substituting an assumed expansion such as Eq. (2.2) into the exact equation and equating powers of $k$. Having done this, one is ready to study the contribution from $r>R$ by the perturbation or iteration method. $R$ is assumed very large, the asymptotic expansion of $U(r)$ is substituted into the equation, and the new variable $x = kr$ is introduced. With $f(R)$ taken as the zero order quantity, the iteration is begun. One then notices that the leading power of $k$ introduced by each succeeding order of perturbation theory is of higher order in $k$ than the last (apart from the renormalizations already discussed), and uses this to decide at which order to stop. Finally, one replaces partially renormalized quantities like the bracket and $A(R)$ in Eq. (2.7) by the fully renormalized quantity, such as $A$. 

(8)
3. EXPANSION OF THE SCATTERING AMPLITUDE, \( f(\theta, \phi) \)

In this section we are interested in the solution of the Schrödinger equation

\[
[V^2 + k^2 - U(r)] \psi_{rad}(r) = 0
\]

with the asymptotic form \( \psi \sim \exp(i k_{\perp} \cdot r) + f(\theta, \phi) \exp(ikr)/r \), where the vector \( k_{\perp} \) is in the direction of the incident plane wave. The non-central potential \( U(r) \) may be represented by a Legendre expansion relative to some z axis

\[
U(r) = \sum_{L \text{ even}} U_L(r) P_L(\cos \theta)
\]  \hspace{1cm} (3.1)

where the \( U_L \) are assumed to have the following asymptotic dependence as \( r \to \infty \),

\[
U_2 \sim q/r^3 - p'/r^4 + o(r^{-5})
\]

\[
U_0 \sim -p/r^4 + o(r^{-5})
\]  \hspace{1cm} (3.2)

and higher \( U_L \), if they exist, are \( o(r^{-5}) \). The reason for the particular asymptotic dependence assumed for the potentials by Eq. (3.2) is that this is the asymptotic form which one finds for the electrostatic interaction of a charged particle with a neutral quantum mechanical system, for example an electron and an atom. In this case the asymptotic form of \( U_2 \) will be proportional to the electric quadrupole moment of the target system, and this
will be the dominant long range interaction if it exists. The $r^{-4}$ term in $U_0$ will be proportional to the target's electrical polarizability. The derivation of the known asymptotic forms Eq. (3.2) for an electron-atom system is indicated in Sec. 4. The restriction of the sum to even terms only is also dictated by the application. Physically this follows from the target system's having a well defined parity. In addition to being non-central, we may allow the potential $U(r)$ to be non-local and energy dependent, provided that the non-locality is of short range and the energy dependence can be represented by an expansion in $k^2$ near $k = 0$. (These points will not be explicitly discussed further.)

In order to apply the method discussed in the preceding section, the Schroedinger equation must first be replaced by the appropriate first order non-linear equation for the quantity of interest, in this case the scattering amplitude, $f(\theta, \phi)$. This equation was found by Spruch to be

$$f_r(k_i, q) = f_r(k_i, q) - (1/4\pi) \int \frac{r'}{r} dr \int d\Omega [e^{i(k_i \cdot r')}/r']$$

$$+ f_{r'}(k, q) e^{ikr'/r'} U(r \cdot [e^{i(k_i \cdot r')}/r'] + f_{r'}(-k, q) e^{ikr'/r'})$$

(3.3)

where the argument, $r$, is now written as a subscript. The vector $k_i$ is again in the direction of the incident plane wave and $k_f$ is a vector in the final direction, or the direction of observation. The vector $k'$ has as its angles the variables $\theta$ and $\phi$ of integration. The lower limit of integration, $r_0$, is arbitrary.

Before looking for the contribution to $f$ from the asymptotic region of the potential, let us first, as in the last section, consider the expansion of $f_r$ for $r$ less than some finite and fixed, though possibly

(10)
large, \( R \). It is easily verified that the appropriate expansion which takes
the place of Eq. (2.2) of the last section is one in powers of \( ik \), namely

\[
f(r) = \sum_{n=0}^{\infty} (ik)^n f_n
\]  

(3.4)

for \( r < R \) fixed. Substituting this in Eq. (3.3) and equating like powers of
\( ik \) one finds the equations for the individual functions, \( f_n \). In particular
the equation for \( f_0 \) is

\[
f_0(r) = -(1/4\pi) \int_0^r r'^2 \, dr' \, [1 + f_o/r]^2 \int d^3u(r')
\]  

(3.5)

where for the present purpose we have set \( r_o = 0 \). Since the angular inte-
gral over the potential simply gives \( 4\pi U_o \), we see that Eq. (3.5) is identi-
cal with Eq. (2.3) for the scattering length (rather for \(-A\)), with the po-
tential given by the spherically symmetric component, \( U_o \). Therefore we shall
refer to the quantity \(-f_o\) as the scattering length and use the notation
\(-f_o = A\). An important property of \( A \) is that it is entirely independent of
the \( L > 0 \) (the non-spherically symmetric) terms in the potential.

The equation for the next function, \( f_1 \), in Eq. (3.4) may similarly
be found. It is more complicated but simplifies when we use the fact that
the potential \( U(r) \) contains only even angular terms. We shall not write
the equation for \( f_1 \), but it is exactly satisfied by the function

\[
f_1(r) = f_o^2(r)
\]  

(3.6)
If we temporarily imagine that the potentials are of short range so that we may go to the limit \( r = \infty \), Eq. (3.6) gives the optical theorem in the zero energy limit. Again we note that Eq. (3.6) explicitly assumes that the potential has no component proportional to \( P_1(\cos \theta) \).

We may now sum up the result of Eqs. (3.4) through (3.6) to write the expansion of the amplitude, \( f_R \), for any finite though possibly very large \( R \), as \( kR+0 \). It is

\[
f_R = -A(R) + ikA^2(R) + O(k^2) \quad .
\]

Eq. (3.7) might have been simply written down immediately as the known contribution to the scattering amplitude due to a potential in the region \( r \) less than some finite \( R \). However it seems more consistent to rederive it in the context of the present method.

We now proceed to our main purpose, namely to seek the contribution to the amplitude \( f \) from the region \( r>R \), using Eq. (3.3) and writing \( r_0 = R \). As in the last section, the arbitrary distance \( R \) will be considered to be very large so that the asymptotic expansion (3.2) of the potential may be used. Accordingly we substitute the potential from (3.1) and (3.2) into Eq. (3.3) and multiply out the two brackets. We again introduce new variables

\[
x = k r' \\
y = K r' = (K/k)x
\]

where \( K \) is the magnitude of the momentum transfer vector, \( K = k_f - k_i \). It is related to \( k \) by \( K = 2k \sin(\theta_{if}/2) \) [see figure 1]. The equation becomes

\[(12)\]
\[
f_{\rho}(k_{\rho}, k_{\omega}) = f_{R}(k_{\rho}, k_{\omega}) - \left(\frac{1}{4\pi}\right) \int_{k_{R}}^{kr} x^2 \, dx \int d\Omega \{ p_{\omega}(\cos\theta) x^{-3} \\
- k x^{-4} [p_{\omega} + p'_{\omega} p_{\rho}(\cos\theta)] + \ldots \} e^{i\nu \cos(\theta; \theta_{k})} + (k/x) f_{R}(k_{\rho}, k_{\omega}) e^{ix[1-\cos(\theta_{1}, \theta)]} + (k/x) f_{\rho}(k_{\rho}, k_{\omega}) e^{ix[1+\cos(\theta_{2}, \theta)]} \\
+ \left(\frac{k^2}{x^2}\right) f_{\rho}(k_{\rho}, k_{\omega}) f_{\rho}(k_{\rho}, k_{\omega}) e^{2ix} \tag{3.9}
\]

where the notation \( \cos(\theta_{1}, \theta_{2}) \) is used here and throughout the paper to denote the cosine of the angle, \( \theta_{12} \), between the vectors \( k_{\omega} \) and \( k_{\rho} \). \( \cos(\theta_{1}, \theta_{2}) \) is given by the relation

\[
\cos(\theta_{1}, \theta_{2}) = \cos\theta_{1} \cos\theta_{2} + \sin\theta_{1} \sin\theta_{2} \cos(\phi_{1} - \phi_{2}) \tag{3.10}
\]

There remains nothing now but to go ahead and evaluate the integrals in Eq. (3.9) by the iteration or perturbation method, beginning with

\[
f_{\rho}^{(0)} = f_{R} = -A(R) + 1 k A^{2}(R) + O(k^2) \tag{3.11}
\]

where the superscript henceforth denotes the order of perturbation theory.

We proceed to sufficiently high order in perturbation theory to obtain all the powers of \( k \) which are desired. As implied in Eq. (3.11) only terms through \( O(k) \) will be sought here. (These will be seen to provide more than sufficient difficulty in evaluating while at the same time furnishing a great deal of detail in the results.)

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By inspection of Eq. (3.9) it may be seen directly to what order in perturbation theory we must go in order to find all terms through $O(k)$, by taking the heuristic point of view explained in the last section of neglecting temporarily the $k$ dependence of the lower limit of integration. Of the four exponential terms in the last bracket, the first term is $O(1)$. This will be called the Born term since it appears also in the Born approximation. Since it is not multiplied by any factor $f$ as are the subsequent terms, it makes its contribution once and for all in first order. It contributes to $f$ a $q$ term of $O(1)$ and $p$ and $p'$ terms of $O(k)$. Higher terms in the potential would give contributions of $O(k^2)$ which is why they have not been written explicitly. Skipping ahead to the last exponential term in the bracket, it is seen that this already contains a factor $k^2$ which makes it higher order from the very beginning, and so it makes no contribution. Finally the two linear $f$ terms in the bracket behave alike. They have a factor of $k$ to start with. Since the lowest order terms in $f^{(0)}$ and $f^{(1)}$ are $O(1)$, the $p$ and $p'$ terms produced by these will always be $O(k^2)$. In first order, these linear $f$ terms will produce $q$ terms of $O(k)$ proportional to $f^{(0)}$. When we set these $f$'s equal to $f^{(1)}$ to obtain the second order result, we see that the Born term proportional to $q$ will result in a $k^2$ term in this order. If the iteration process is continued further, it is seen that only terms of $O(k^2)$ are produced and so second order suffices.

We now proceed to evaluate the first order contribution, $f^{(1)}$ to the amplitude. First, the zero order quantity, $f^{(0)}$, given by Eq. (3.11) is substituted for $f$ on the right hand side of Eq. (3.9). The angular integrations are easily performed using the relation

$$\int d\Omega_L^{(s)}(\cos \theta) e^{ix \cos (\theta, \theta_k)} = 4\pi i^L J_L(x) P_L^{(s)}(\cos \theta_k)$$  \hspace{1cm} (3.12)
This reduces Eq. (3.9) to

\[
\begin{align*}
\mathcal{F}_k^{(1)}(k_f + k_f) &= [-A(R) + i k A^2(R)] = p_2(\cos \theta_K) \frac{k R}{q} \int_0^{k R} dx x^{-1} j_2(y) \\
&\quad + q k A(R) \left[p_2(\cos \theta_f) + p_2(\cos \theta_f)\right] \int_0^{k R} dx x^{-2} e^{i x} j_2(x) + O(k^2), \quad (3.13)
\end{align*}
\]

The lower limit of integration has been extended to zero whenever the error introduced into \( f \) thereby was \( O(k^2) \). The first three terms, resulting from the Born term in Eq. (3.9) are complicated by the presence of two different variables, \( x \) and \( y \). It is easiest to eliminate the variable \( x \) in favor of \( y \) by use of Eq. (3.8). In the first integral, this merely changes the limits \((k R, k R)\). In the second and third it also replaces the initial factor \( k \) by \( K \).

Before proceeding to second order, let us look at the physical amplitude, \( f_{\infty}^{(1)} \) in this order. Letting \( r = \infty \), we have

\[
\begin{align*}
f_{\infty}^{(1)}(k_f + k_f) &= -[A(R) - \frac{p}{R}] + (1/3) q p_2(\cos \theta_K) - (1/4) \pi p K \\
&\quad - (\pi/16) q' k K p_2(\cos \theta_K) + ik \left[A^2(R) - (1/12) A(R) q \left[p_2(\cos \theta_f) + p_2(\cos \theta_f)\right]\right] \\
&\quad + O(k^2)
\end{align*}
\]

The first term on the right is of course the scattering length, partially renormalized in first order. The second term represents the principle new result of the paper, a term generated by the quadrupole potential
which is 0(1) but with angular dependence. As in previous work, this leading term given by the Born integral. The angular factor \( P_2(\cos \theta_K) \) requires some explanation. The angle \( \theta_K \) is not the scattering angle. It is the angle made with the z axis by the momentum transfer vector \( K = k_i - k_f \) (the magnitude, \( K \), of this vector appears in the following term). The vector \( K \) is represented in Fig. (1). The magnitude \( K \) is given (since \( |k_i| = |k_f| = k \)) by the familiar relation \( K = 2k \sin(\theta_{if}/2) = k \sqrt{2}(1 - \cos(\theta_i, \theta_f))^{1/2} \). The quantity \( \cos \theta_K \) can be found from the relation

\[
\cos(\theta_K) = \frac{K_z}{K} = \frac{\cos \theta_i - \cos \theta_f}{\sqrt{2}(1 - \cos(\theta_i, \theta_f))^{1/2}} \tag{3.15}
\]

The denominator might in turn be eliminated in favor of the angles \( \theta_i, \theta_f \) and \( \phi_i - \phi_f \) by the relation \( \cos(\theta_i, \theta_f) = \cos \theta_i \cos \theta_f + \sin \theta_i \sin \theta_f \cos(\phi_i - \phi_f) \). So if the initial angle \( \theta_i \) is arbitrary relative to the z axis from which the quadrupole potential is measured, the amplitude will depend on \( \phi \) as well as \( \theta \). Now for the special case \( \theta_i = 0 \), Eq. (3.15) reduces to

\[
\cos \theta_K = \sin(\theta/2) \quad (\theta_i = 0)
\]

where we have written \( \theta_f = \theta \). \( P_2(\cos \theta_K) \) is then given by

\[
P_2(\cos \theta_K) = P_2[\sin(\theta/2)] = (1/4)(1 - 3\cos \theta) \quad (\theta_i = 0) \tag{3.16}
\]

The third term in Eq. (3.14) is the known term \( r^{-4} \) giving the lowest order effect of the \( r^{-4} \) potential. As a consistency check, if one considers the case \( \theta_i = 0 \), the imaginary terms for \( \theta_f = 0 \) may be deduced from the two leading (real) terms by means of the optical theorem and they agree with those in Eq. (3.14).
Now, to proceed to second order, we substitute $f_r^{(1)}$ from Eq. (3.13) with the required changes of angles back into the right hand side of Eq. (3.9). The leading term in $f_r^{(1)} - f_r^{(0)}$ is the first $q$ term in (3.13) which is $O(1)$. This term multiplied with the $q$ term in the potential will give a $q^2 k$ term as mentioned above. All other terms are $O(k^2)$ and hence higher order (except for second order corrections to the scattering length arising from the $p$ terms). Since further iterations may be seen to produce only higher order terms, $f_r^{(2)}$ is as high in perturbation theory as we shall go, and so, letting $r \to \infty$, we find

$$f_r^{(2)}(k \to k', \omega) - f_r^{(1)}(k \to k', \omega) = - \frac{1}{4\pi} \int_{kR}^{\infty} x^2 dx \int \Omega(q/x^3) P_2(\cos \theta)$$

$$\times \left( \frac{k}{x} \right) \frac{q}{P_2(\cos \theta_k)} \left[ \frac{1}{3} - \frac{j_{1}(k'r')}{k'r'} \right] e^{i x [1 - \cos (\theta_k, \theta)]}$$

$$+ \frac{(k \to k', \omega)}{x^{1/2}} + O(k^2)$$

(3.17)

where, according to the requirements of Eq. (3.9), $\theta_k$ is defined as the angle made with the $z$ axis by the vector $K' = k_i - k'$. An analysis like that leading to Eq. (3.15) for $\theta_k$ gives

$$\cos \theta_k = \frac{\cos \theta_i - \cos \theta}{\sqrt{2} [1 - \cos (\theta_i, \theta)]^{1/2}}$$

(3.18)

while the magnitude $K'$ is equal to $k \sqrt{2} [1 - \cos (\theta_i, \theta)]^{1/2}$. The corresponding quantities for $(k \to k', \omega)$ should be clear. The $r'$ should be eliminated by the relation $K'r' = (K'/k) x$. At this point it does not seem that the integrations in Eq. (3.17) can be carried out analytically, so we will simply write

(17)
\[ f_\infty^{(2)} - f_\infty^{(1)} = q^2 k I(\theta, \phi) + 0(k^2) \quad (3.19) \]

where

\[
I(\theta, \phi) = -\left(\frac{1}{4\pi}\right) \int_0^\infty dx x^{-2} e^{ix} \int d\Omega_2 \cos\theta \ p_2(\cos\theta, \phi, \theta, \phi) \\
\times [1/3 - i_1(K'\tau)/K'\tau] \ e^{ix} \cos(\phi - \theta) + (k_i \leftrightarrow -k_f)
\]

\[
= (4\pi)^{-2} \int_0^\infty d\tau x^{-2} x^{-4} e^{ix} e^{-ix} \cos(\phi - \theta) \ p_2(\cos\theta) \\
\times [1/3 - i_1(K'\tau)/K'\tau] \ e^{ix} \cos(\phi - \theta)
\]

\[+ (k_i \leftrightarrow -k_f) \quad (3.20) \]

I(\theta, \phi) has been written in the alternate form of a double integral from which it arose, since it might prove more amenable to solution in this form. At any event it should be possible to evaluate the integrals numerically for various values of \( \theta_f \) and \( \phi_f \) if it is ever needed. The angle \( \theta_{k''} \) represents the vector \( K'' \), which is the difference between the vectors \( k_{i''} \) and \( k' \), the latter having the angles \( \theta' \) and \( \phi' \) of integration. I(\theta, \phi) should of course have both a real and an imaginary part.

As mentioned earlier, an evaluation of \( f^{(3)} \) leads only to terms of \( 0(k^2) \) aside from further renormalizations of the scattering length, \( A \). The final result then may be written, combining Eqs. (3.19) and (3.14),

(18)
\[
\begin{align*}
&f(k_{i} \rightarrow k_{f}) = -A + (1/3) q \ p_{2}(\cos \theta_{K}) - \frac{1}{4\pi} \ p \ K + q^{2} \ k \ Re I(\theta, \phi) \\
&- (\pi/16) \ p \ k \ p_{2}(\cos \theta_{K}) + i \ k \ \left[ A^{2} - \frac{1}{12} q A \ (p_{2}(\cos \theta_{f}) + p_{2}(\cos \theta_{i})) \right] + q^{2} \ Im I(\theta, \phi)] + O(k^{2})
\end{align*}
\]

(3.21)

where the renormalized quantity, \( A = A(\infty) \) has been substituted throughout, and \( \theta_{K} \) may be found from Eq. (3.15), ff. Eq. (3.21), the final result of this section represents the expansion of the scattering amplitude through terms linear in \( k \) for the potential of Eqs. (3.1) and (3.2). An attempt will be made in Sec. 4 to apply this result to low energy electron-atom scattering.
Dipole Potential

As a digression, let us attempt to apply the above method to a potential whose asymptotic form contains a leading dipole term

$$U(r) \sim D \cos(\theta) / r^2$$

(3.22)

(This kind of potential arises in connection with the scattering of electrons from the excited states of the H atom, because of the accidental degeneracy between states of different angular momentum.) We substitute this asymptotic form into Eq. (3.3), neglecting any higher order terms in $U$ since we shall only look for the leading $k$ term in $f(\theta)$. In addition, we again substitute the new variables $kr' = x$ and $Kr' = y$, and multiply through by a factor $k$. We find in place of Eq. (3.9)

$$k f_y (k \rightarrow k)^{R} = f_R - (1/4\pi) \int \frac{kr}{kR} x^2 dx \int d\Omega D \cos(\theta) x^{-2}$$

$$\chi [e^{ix} \cos(\theta, \theta_K) + x^{-1} k f_x (k \rightarrow k') e^{ix} e^{-ix} \cos(\theta, \theta_F)]$$

$$+ x^{-1} k f_x (-k \rightarrow k') e^{ix} e^{ix} \cos(\theta, \theta_F)$$

$$+ x^{-2} k f_x (k \rightarrow k') k f_x (-k \rightarrow k') e^{2ix}$$

(3.23)

Now by Eq. (3.11) $f_R$ is $O(1)$. (As mentioned before the $1k$ term would be different for a dipole potential, but this is a higher order term anyway.) So $k f_R$ is $O(k)$. Let us neglect terms of $O(k)$ as higher order and look only for terms of lower order than this. We then have $k f^{(0)} = O(k)$. Using this on the right hand side we find for $f^{(1)}$
\[ \text{k } f^{(1)}(k, k_F) = -(D/4\pi) \int \frac{kr}{kR} \, dx \int d \Omega \cos \theta \, e^{iy \cos(0, 0_k)} + O(k) \]

\[ = -iD \frac{k}{K} \cos \theta \left[ 1 - f_o(y) \right] + O(k) \quad (3.24) \]

Thus, in first order, \( k f \) is \( O(1) \) as we could see by inspection of (3.23). If we now proceed to substitute \( k f^{(1)} \) on the right hand side in order to find \( k f^{(2)} \), we see immediately that the new terms are also \( O(1) \) and so to all higher orders of perturbation theory. So that the situation here is very different from that for an \( r^{-3} \) or \( r^{-4} \) potential, where the new terms in higher orders of perturbation theory represented successively higher powers of \( k \). With the dipole potential, all orders of perturbation theory give the same power of \( k \), namely \( f = k^{-1} \). Thus for the dipole potential, Eq. (3.24) (for \( y = \infty \)) gives only the first Born approximation to the \( k^{-1} \) term in \( f(\theta) \), and so will only be of use if \( D \) happens to be very small. For moderate \( D \) higher order perturbation terms would be needed, while for still higher \( D \) the expansion will very likely not converge at all.

So we see that unfortunately the present method breaks down for a potential which falls off as slowly as \( r^{-2} \). From Eq. (3.24) we may at least salvage the qualitative result that the amplitude diverges as \( k^{-1} \) in agreement with the classical result \(^{10} \), and also with that of Seaton \(^{11} \) who considered the electron-hydrogen problem for a fixed value of the total angular momentum, \( L \), and with Gailitis and Damburg \(^{12} \) who carried this result somewhat farther. If one wishes to go beyond the Born approximation or the contribution to the amplitude from single angular momentum states, what seems to be needed is an exact solution of the wave equation with the dipole potential (3.22).
IV ELECTRON - ATOM SCATTERING

The particular asymptotic form of the potential $U(r)$ given by Eq. (1.1) was chosen because it corresponds to the long range interaction between a neutral atom (or molecule) in a particular state and a charged particle (electron).

The potential between an atom and an electron is taken (neglecting spin dependent forces) to be the sum of all Coulomb forces between particles (electrons and nucleus). When the separation, $r$, is very large, the interaction assumes the asymptotic form

$$V(r, \mathbf{r}_j) \sim \sum_{L=1}^{\infty} \frac{2 e^2}{r^{L+1}} \sum_{j=1}^{Z} \frac{L}{L} P_L[\cos(\theta, \theta_j)]$$

(4.1)

where $Z$ is the atomic number of the atom, $r$ and $\theta$ are the coordinates of the separated electron, and $\mathbf{r}_j$ represents the position of the $j$th atomic electron. The absence of an $L=0$ term results from the assumed neutrality of the atom. From this, the limiting form Eq. (1.1) of the effective potential seen by the scattered electron has been derived by a number of authors.

The simplest way to derive an effective potential is to treat the asymptotic potential (4.1) as a perturbation of the atomic ground state and to find its expectation value in first and second order perturbation theory, treating $r$ as a (large) parameter. If we assume the atom to be and to remain in a particular state of magnetic quantum number $M$, the first order result is

$$V_{00} \sim \sum_{L=1}^{\infty} \frac{\ell_{L}(M) P_{L}(\cos \theta)}{r^{L+1}}$$

(4.2)
where the $Q_L(M)$ are the permanent electric multipole moments of the atom in its ground state with quantum numbers $J$ and $M$. Only those moments will exist for which $L \leq 2J$, so that for example a spherically symmetric atom will have no permanent moments. Further, since all atoms in their ground states have a well defined parity, all the odd moments vanish so that the leading term in (4.2) is that for $L = 2$, the quadrupole term. This immediately gives us the first term of Eq. (1.1). The $M$ dependence of the quadrupole moment is given by

$$Q(M) = \frac{3M^2 - J(J+1)}{J(2J-1)} Q$$  \hspace{1cm} (4.3)

where the number $Q$ is defined as the expectation value of the quadrupole operator for the state $M = J$,

$$\frac{1}{2} Q = e \int dr \sum_{j=1}^{Z} r_j^2 P_2(\cos \theta_j) |\psi_{M=J}|^2$$  \hspace{1cm} (4.4)

with the integral extending over all the coordinates of the atom (a sum over spins is implied). Eq. (4.3) has as a consequence that the average of $Q(M)$ over $M$ vanishes

$$Q_{av} = 0$$  \hspace{1cm} (4.5)

Unfortunately the physical situation is somewhat more complicated. Due to the degeneracy of states with the same magnetic quantum number $M$, transitions between these states may be caused by electrons with vanishingly small energy, so that the first order potential should really be written as

$$\mathcal{V}(M) = e \int dr \sum_{j=1}^{Z} r_j^2 P_2(\cos \theta_j) \langle \psi_{M=J} | \mathcal{V} | \psi_{M=J} \rangle$$  \hspace{1cm} (4.6)
a matrix of dimension 2J+1. What has been done in (4.2) is to neglect all but "elastic" collisions, i.e., those in which M remains constant. This neglect is not justified, and an attempt is made below to remedy it.

Returning to Eq. (4.1) and evaluating it now in second order perturbation theory gives

\[ V^{(2)} = e^2 / (2r^4) [a + a'(M) P_2(\cos \theta)] + O(r^{-6}) \]  

where \( a \) is the (average) electric polarizability of the atom and \( a' \) (which exists only for non-symmetric atoms) has the property that, like the quadrupole moment, its average over \( M \) vanishes. In evaluating this result, the variable \( r \) is treated as a constant parameter. This is known as the adiabatic approximation. However, it has been shown\(^1\) that the result gives the correct asymptotic behavior of the effective potential, in other words that the adiabatic approximation is correct asymptotically. This gives rise to the second term in Eq. (1.1).

A more consistent and satisfying way of arriving at the long range electron-atom potential is to start from the exact one body optical potential equation\(^1\) for an electron scattered from an atom in its ground state

\[ [V^2 + k^2 - (2m\hbar^2) V_{\text{opt}}] u(r) = 0 \]  

where

\[ V_{\text{opt}}(r) = V_{00} + \langle \psi_{\text{target}} | (E - H)^{-1} \psi_{\text{target}} \rangle \]  

\( V_{00} \) is the expectation value of the full electron-atom potential averaged over the target ground state. It corresponds exactly with the first order
perturbation theory result whose asymptotic form is given in Eq. (4.2) and the same comments made there again apply. In the second term, the vector \( \mathbf{V} \) has as its components the matrix elements \( V_{01} \) connecting the target ground state with each of its excited states. Similarly the matrix \( H \) has components \( H_{ij} \) connecting any 2 excited states of the atom (but with no ground state components). The Pauli principle may be considered to be implicit in (4.8) or else exchange terms may be added explicitly. In either case it may easily be shown that its effects fall off exponentially as \( r \to \infty \) and so will not affect the asymptotic behavior of \( V_{0\text{opt}} \).

Now if one lets \( r \to \infty \) in Eq. (4.8) using (4.1) for the potential one obtains in a straightforward manner Eq. (4.6) as the limiting form for the second term but with error this time \( O(1/r^5) \). And so the asymptotic form of the optical potential (with the restriction mentioned below to "elastic", i.e., \( M \) conserving, collisions) is

\[
\frac{2m}{\hbar^2} V_{\text{opt}} \sim \frac{O(M)}{a_{\text{o}}} \frac{P_2(\cos \theta)}{r^3} - \frac{1}{a_{\text{o}}^4} \left[ a + a'(M)P_2(\cos \theta) \right] + O(\frac{1}{r^5}) \quad (4.9)
\]

where \( a_{\text{o}} = \frac{\hbar^2}{me^2} \) is the electron Bohr radius. Comparing Eq. (4.9) with Eq. (1.1) we see that in applying the formulas of Sec. 3 to this case we should set

\[
q = \frac{O(M)}{ea_{\text{o}}} , \quad p = \frac{a}{a_{\text{o}}} , \quad p' = \frac{a'(M)}{a_{\text{o}}} . \quad (4.10)
\]

The foregoing, however, is not really adequate to describe the scattering of electrons by atoms, since transitions of the atom from one magnetic state to another have not been taken into account.
Allowance for Transitions Between Magnetic States

If the target atom is initially in a magnetic state $M$ relative to some z axis, and an electron beam is incident with momentum $k$, the asymptotic form of the wave function may be written

$$\psi \sim \psi_{M',M}(r) e^{ik\cdot r} \sum_{M''=M'} \frac{f_{M,M'}(\theta,\phi) \psi_{M''}(r)}{r^{J+1}} e^{ikr/r} \quad (4.11)$$

where $\psi_{M,M'}(r)$ are the ground state wave functions for the atom in the magnetic state $M'$. The amplitude $f(\theta,\phi)$ is now a matrix of dimension $2J+1$, connecting these states. Correspondingly the potential $V_{00}$ of Eq. (4.8) is likewise a matrix, as mentioned earlier. If the matrix elements of the potential $V_{00}$ connecting the states $M$ and $M'$ are labeled $V_{00}(M,M')$, where $V$ is still given by Eq. (4.1) the asymptotic form of the potential matrix elements is given by

$$V_{00}^{M,M'} \sim r^{-3}(4\pi/5)^{1/2} r_{2s,M-M'}(\theta,\phi) \left( Q_{M,M'}/(e\alpha) \right) + O(r^{-5}) \quad (4.12)$$

where

$$\frac{1}{2} Q_{M,M'} = e(4\pi/5)^{1/2} \int d\tau^* \psi_{M'} Z \sum_{j=1}^Z r_{2s,M-M'}(\theta_j,\phi_j) \psi_{M} \quad (4.13)$$

The $Q_{M,M'}$ are related to the ordinary quadrupole moment, $Q = Q_{J,J}$ by the relation

(26)
\[ Q_{M,M'} = \left( \frac{(J+1)(2J+3)}{J(2J-1)} \right)^{1/2} C(J,2,\bar{J};M',M-M') Q \]  \hspace{1cm} (4.14)

where \( Q \) is the quadrupole moment defined by Eq. (4.4), and \( C \) is the Clebsch-Gordon coefficient. The \( Q(M) \) defined before are simply the diagonal elements, \( Q_{M,M} \).

The second term of the optical potential is still \( O(r^{-4}) \), so that Eq. (4.12) represents the leading term in the optical potential matrix as \( r \to \infty \). If the amplitudes \( f_{M,M'}^{(M)} \) are now written as functions of \( r \) as was done in Sec. 3 for \( f \), they satisfy coupled equations which are therefore more complicated than Eq. (3.3). These equations will not be written down here. However, if we are satisfied with terms in the amplitudes of \( O(1) \), we see that these were given in Sec. 3 by the Born term in Eq. (3.3), together with the \( r^{-3} \) term in the potential, apart from contributions from the short range part of the potential. The same will be true in the present case.

The Born term for the \( f_{M,M'} \) is easily written down and evaluated, with the potential given by Eq. (4.12). It is

\[ f_{M,M'}^{(M)}(k \to k_f) = f_{M,M'}^{(M)}(R) - \frac{1}{4\pi} \int_R^\infty r^2 dr \int d\Omega \ e^{i\mathbf{K} \cdot \mathbf{R}} \frac{1}{r^3} \left( \frac{4\pi}{5} \right)^{1/2} Y_{2,M-M'}(\theta,\phi) \]

\[ \times \frac{Q_{M,M'}}{e a_o} + O(k) \]

\[ = -A \delta_{M,M'} + \frac{1}{3} \frac{Q_{M,M'}}{e a_o} \left( \frac{4\pi}{5} \right)^{1/2} Y_{2,M-M'}(\theta,\phi) + O(k) \]  \hspace{1cm} (4.15)

\( K \) is again the momentum transfer vector, \( k_f - k \), \( A \) has the same meaning as in Sec. 3, and the substitution of \( A \) for \( A(R) \) has again been made as in
Sec. 2 and 3. The relation of $\theta_K$ to the angles of $k_L$ and $k_F$ was given by Eq. (3.15). Similarly $\tan \phi_K = K_x/K_y$ and this is equal to

$$\tan \phi_K = \frac{\sin \theta_1 \sin \phi_1 - \sin \theta_F \sin \phi_F}{\sin \theta_1 \cos \phi_1 - \sin \theta_F \cos \phi_F}.$$  \hspace{1cm} (4.16)

The delta function arises from the fact that the (scattering length) equation which determines the leading term of $f_R$ contains only the angular average of the potential and so does not connect states of different $M$.

Eq. (4.15) represents the final result of this section, the scattering amplitude to lowest order in $k$ for collisions of very slow electrons with a non-symmetric atom initially in magnetic state $M$. We shall now mention two obvious applications of this formula. The first is the scattering of slow electrons from unoriented atoms. For this case one should construct the cross sections and then average over initial states $M$ and sum over final states $M'$. Using Eq. (4.14) for $\Omega_{M,M'}$ we find

$$\sigma(\theta)_{av} = \frac{1}{2J+1} \sum_M \sum_{M'} |f_{M,M'}|^2 = A^2 + \frac{1}{9} \left( \frac{\Omega}{\epsilon a_0} \right)^2 \frac{(J+1)(2J+3)}{5J(2J-1)} + O(k)$$  \hspace{1cm} (4.17)

where $J$ is the total angular momentum of the atom$^{22}$. We have used the sum rules for spherical harmonics and for Clebsch Gordon coefficients$^{23}$ together with Eq. (4.5). It should be noted that the differential cross section given by Eq. (4.17) is spherically symmetric.

If the target atoms have been oriented so that they are initially in magnetic state $M$, then Eq. (4.15) may be used directly to determine the differential cross section for transitions to any other state $M'$ caused by
collisions with very slow electrons. In this case, changes \( A^M \) by 0, 1, and 2 units are allowed. To find the total cross sections for these transitions, the integrals over \( \phi_f \) and \( \theta_f \) may be done \(^{24}\), after substituting Eq. (3.15) for \( \theta_k \), giving

\[
\sigma_{M,M} = 4\pi A^2 - \frac{2\pi}{3} A \frac{Q_{M,M}}{e a_0} P_2(\cos \theta_1) \\
+ \frac{1}{9\pi} \left( \frac{Q_{M,M}}{e a_0} \right)^2 \left[ 1 - \frac{3}{8} (\sin \theta_1)^4 \right] + 0(k)
\]

\[
\sigma_{M,M+1} = \frac{1}{12\pi} \left( \frac{Q_{M,M+1}}{e a_0} \right)^2 \left[ 1 + \frac{1}{3} (\cos \theta_1)^4 \right] + 0(k)
\]

\[
\sigma_{M,M+2} = \frac{5}{48\pi} \left( \frac{Q_{M,M+2}}{e a_0} \right)^2 \left[ 1 - \frac{2}{5} (\cos \theta_1)^2 - \frac{1}{15} (\cos \theta_1)^4 \right] + 0(k)
\]  \(4.18\)

These total cross sections still depend on the angle \( \theta_1 \) between the direction of the incident electron and the \( z \) axis along which the atoms have been oriented.

Finally with regard to the energy range of validity of Eq. (4.15) and the results of Sec. 3, as in previous work \(^4\) necessary conditions can be found for the energy. In the iteration process begun in Sec. 3 and implied in the work of the present section, the iterated quantities consisted of the terms \( qk \) and \( pk^2 \) each multiplied by a factor of order unity. Necessary conditions then on the applicability of the preceding results is that dimensionless quantities \( kQ/ea_0 \) and \( k^2 a/a_0 \) be small compared to unity. The latter condition is that already found for the polarization potential.

(29)
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References


5 An alternate approach might be to look for an expansion of the elements of the reactance matrix connecting states of different angular momentum. If one is interested in the scattering amplitude only, this approach is more complicated. But as other information in addition to the scattering amplitude can be found this way, work along this line is being done.


7 The only exception to this is the excited states of the H atom, where there is degeneracy between states of different angular momentum.

8 Reference 6, p. 209.


14 Reference 9, p. 152, ff.

15 This is generally true of excited states as well with hydrogen being an important exception.


17 We have used the definition of Blatt and Weisskopf. The molecular definition of the quadrupole moment used by Cerjuoy and Stein (Reference 13) can be made to agree with this by the relation, \( Q = - \frac{3}{2J(2J+3)} Q_{GS} \).


22 It is interesting to compare the above result with those of Gerjuoy and Stein, Reference 13, although they were not concerned with elastic scattering. If one nevertheless sets \( J_b = J_a \) in their results and \( k_b = k_a \) and uses the relation between the quadropole moments mentioned in Reference 17, one reproduces the second term of Eq. (4.17). (There is of course no \( \lambda^2 \) term in these results since they did not consider elastic scattering.)

23 See Reference 21 (Rose), pp. 60 and 34.

Fig. 1. Shows schematically the meaning of the angle $\theta_K$. 

(34)